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Authors	Fan, Fanghui;Mou, Tian;Nurhadi, Bambang;Roos, Yrjö H.
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Corresponding Author: Professor. Yrjo H Roos,

Corresponding Author's Institution: University College Cork

First Author: Fanghui Fan

Order of Authors: Fanghui Fan; Tian Mou; Bambang Nurhadi; Yrjo H Roos

Abstract: Water sorption-induced crystallization, α -relaxations and relaxation times of freeze-dried lactose/whey protein isolate (WPI) systems were studied using dynamic dewpoint isotherms (DDI) method and dielectric analysis (DEA), respectively. The fractional water sorption behavior of lactose/WPI mixtures shown at $a_w \leq 0.44$ and the critical a_w for water sorption-related crystallization ($a_w(cr)$) of lactose were strongly affected by protein content based on DDI data. DEA results showed that the α -relaxation temperatures of amorphous lactose at various relaxation times were affected by the presence of water and WPI. The α -relaxation-derived strength parameter (S) of amorphous lactose decreased with a_w up to 0.44 a_w but the presence of WPI increased S . The linear relationship for $a_w(cr)$ and S for lactose/WPI mixtures was also established with $R^2 > 0.98$. Therefore, DDI offers another structural investigation of water sorption-related crystallization as governed by $a_w(cr)$, and S may be used to describe real time effects of structural relaxations in noncrystalline multicomponent solids.

1 Water sorption-induced crystallization, structural relaxations and strength analysis of
2 relaxation times in amorphous lactose/whey protein systems

3

4 Fanghui Fan¹, Tian Mou², Bambang Nurhadi¹ and Yrjö H. Roos¹ *

5 ¹ School of Food and Nutritional Sciences; ² School of Mathematical Sciences,

6 University College Cork, Cork, Ireland.

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26 * Corresponding author. E-mail address: yrjo.roos@ucc.ie (Y.H. Roos). First author. E-mail
27 address: fth11235813@gmail.com (F. Fan).

1. Introduction

Water is of key importance to food systems affecting processing, microbial safety, sensory perception, and a storage stability and shelf life (Al-Muhtaseb, McMinn, & Magee, 2002; Lodi & Vodovotz, 2008). Water sorption may be affected by time-dependent phenomena, structural transformations, and phase transitions of food solids. Such transitions may affect rates of deteriorative changes and decrease the storage stability of dehydrated foods, e.g., powdered milk (Silalai & Roos, 2011), potato flakes (Turner et al., 2006), and dry pasta (Aguilera, Chiralt, & Fito, 2003; Gowen, Abu-Ghannam, Frias, & Oliverira, 2008). Water sorption isotherms are important to numerous applications, e.g., development of new products (Wang & Brennan, 1991), determination of product stability and shelf life (Jouppila & Roos, 1994), and process design and control (Peng, Chen, Wu, & Jiang, 2007). The dynamic dewpoint isotherm (DDI) method was developed to generate water sorption isotherms using single samples in a dynamically changing water vapor pressure (Yuan, Carter, & Schmidt, 2011). The DDI method developed along with dynamic vapor sorption provides a continuous measurement of water content (c_w) and water activity (a_w). DDI differs from standard saturated salt solution methods (SSM), which measure c_w for equilibrated materials at known a_w (Schmidt & Lee, 2012). Also, DDI makes it possible to generate complete dynamic isotherms with 50 to 200 data points quickly and accurately without long equilibration times which are typical of SSM methods (Yuan et

49 al, 2011 ; Schmidt & Lee, 2012). Therefore, DDI method offers another real-time
50 investigation of water sorption-related material properties, i.e., crystallization and
51 deliquescence (Yao et al., 2011), in food processing as well as for the control of storage
52 stability and shelf life of resultant products.

53

54 Water sorption characteristics, as well as other interactions of food solids with water,
55 are defined by composition of nonfat components, i.e., carbohydrates and proteins
56 (Roos & Drusch, 2015). Characterization of glass formation of complex food solids
57 systems has been of particular interest in recent years (Ibach & Kind, 2007; Babu &
58 Nangia, 2011). Amorphous food materials exist in a supercooled and non-equilibrium
59 state below their respective equilibrium melting temperature with no well-defined
60 structure. The nonequilibrium state may exhibit an indefinite number of glass structures
61 with varying levels of molecular packing and order. When temperature increases to
62 above glass transition temperature (T_g), a rapid increase of molecular mobility occurs
63 and the glass-forming material transforms to a viscous liquid, which dramatically
64 affects various physicochemical properties of food solids (Slade, Levine, & Reid, 1991;
65 Bhandari & Howes, 1999). Structural relaxations in amorphous food materials around
66 or above the glass transition occur as a result of molecular mobility changes due to
67 variations in external thermodynamic conditions e.g., pressure and temperature. Glass
68 transition may also result internally in materials because of changes in plasticizer or

69 solvent contents, e.g., water, which can induce dramatic changes in solids properties
70 and directly affect processing, storage, bioavailability, and delivery properties of food
71 materials (Yu, Li, & Sun, 2001; Roos & Drusch, 2015). Relaxation times (τ)
72 correspond to the kinetically impeded and time-dependent molecular rearrangements
73 that are responsible for solids structure and properties, e.g., flow characteristics,
74 viscous flow and collapse, mechanical or dielectric properties, and crystallization
75 (Sperling, 2005). Such properties may be used to control the quality and stability of
76 food materials during processing and storage (Champion, Le Meste, & Simatos, 2000).

77

78 The α -relaxation and relaxation times of glass forming food materials around
79 calorimetric T_g could be studied and determined by dielectric analysis (DEA) (Moates,
80 Noel, Parker, & Ring, 2001; Clerjon, Daudin, & Damez, 2003). The α -relaxation
81 temperature (T_α) may also be taken from the dielectric loss (ϵ'') peak temperature at
82 various frequencies to obtain corresponding relaxation times (Silalai & Roos, 2011).
83 The Williams-Landel-Ferry (WLF) model is often used to model relaxation times of the
84 non-Arrhenius temperature dependence of relaxation processes occurring above T_g ,
85 and the τ is shown against $T-T_g$ (Slade, Levine, & Reid, 1991). The WLF-relationship
86 applies over the temperature range covering the rubbery or supercooled liquid state and
87 it was also used to describe time and temperature dependent behavior of food solids
88 systems. The “strength” concept and strength parameter (S) developed by Roos and

others (2015) combined the characterization of material state and relaxation times to describe the critical temperature difference at which a sharp change in properties of the material occurs. On the other hand, the S parameter based on WLF modeling was used to describe amorphous food solids and their properties for typical processing and storage conditions where a component or miscible components within food structure may experience the glass transition (Fan & Roos, 2016a). Besides the strength of food solids, the Deborah number was applied to provide a useful translation of measured relaxation times to real timescales. Therefore, the strength concept gives a quantitative measure to estimate compositional effects on relaxation times to describe properties of food solids above measured T_g .

Lactose (β -D-galactopyranosyl (1–4)-D-glucopyranose) is one of the most common and important ingredients in many formulated foods and pharmaceutical materials, and it exhibits strong water-dependent properties, i.e., glass transition and crystallization from its amorphous states during storage (Nickerson, 1979; Gänzle, Haase, & Jelen, 2008). Understanding glass transition-related structural relaxations and their coupling with water sorption properties is essential for modeling the physical state of dairy-based food systems at various conditions and the design of complex formulations. The importance of glass transition to amorphous solids characteristics has been well recognized but few studies have contributed to understanding effects of glass former or

polymer, i.e., protein, on the water sorption characteristics and structural relaxations in food formulations. Therefore, the major objective of the present study was to investigate the influence of food polymeric components (whey protein isolates, WPI) on the water sorption properties of freeze-dried amorphous lactose/WPI mixtures using the DDI measurement data at 25 °C. The strength analysis was carried out to determine the S parameter for lactose/WPI systems by analyzing their relaxation times measured by DEA after storage at $a_w \leq 0.44$ a_w and 25 °C. These data are useful for the understanding of the effects of proteins on water sorption properties of amorphous lactose and collective structural relaxation behavior when present with amorphous lactose around the glass transition in well-mixed food and pharmaceutical materials.

2. Materials and Methods

2.1. Sample preparation

α -Lactose monohydrate (>99 % lactose) (Sigma-Aldrich, St. Louis, Mo., U.S.) and whey protein isolate (WPI; Isolac[®], Carbery Food Ingredients, Co., Ballineen, Ireland; minor components including carbohydrates or lipids < 3%) were used. Aqueous lactose and WPI with 20 % (mass) solids at room temperature were used to obtain ratios of 7:3, 1:1 and 3:7 of lactose/WPI by mass. Mixed solutions (5 mL in total) were prepared in pre-weighted glass vials (10 mL; Schott Müllheim, Germany). All solutions in the vials

(semi-closed with septum) were frozen at -20 °C for 20 h and then subsequently tempered at -80 °C for 3 h prior to freeze-drying using a laboratory freeze-dryer (Lyovac GT2 Freeze-Dryer, Amsco Finn-Aqua GmbH, Steris®, Hürth, Germany). After freeze-drying at pressure < 0.1 mbar, triplicate samples of each material were stored in evacuated desiccators over P_2O_5 at 25 °C (Sigma-Aldrich, St. Louis, Mo., U.S.) prior to subsequent analysis.

2.2. Water sorption experiment

The water sorption of freeze-dried samples was studied using an AquaSorp isotherm generator (AIG; Decagon Devices, Inc. Pulman WA, USA). The airflow continuously passes over the sample in AIG until certain interval time or when there was a mass or a_w change of sample, then the flow stopped and the snapshot of the sorption process was taken by directly measuring mass and a_w based on a high precision magnetic force balance and chilled-mirror dewpoint sensor (Decagon Devices, Inc. Pulman WA, USA). Based on above principle the dynamic water sorption of DDI can be comparable to real-time sorption process for a material with fast vapor diffusion or by reducing the sample size. In the present study, approximately 600 mg of each sample (dried powder), which could cover the bottom of stainless steel sample cup, was used in measurements. Measurement parameters were 0.05 to 0.90 a_w at a temperature of 25 °C,

airflow of 300 ml/min (Schmidt & Lee, 2012). At certain interval time, the airflow stopped automatically then the weight change and the a_w of the sample were recorded. After initial c_w was determined, the mass was converted to the c_w of the sample at the corresponding a_w and a plot of the dynamic sorption isotherm using the SorpTrac software, version 1.03.3 (Decagon Devices, Pullman, WA, USA) was generated. Since each DDI run is unique, the sorption section of the working isotherm was obtained in duplicate, each on a different sample.

Fig 1.

The critical a_w value for water sorption-induced crystallization ($a_w^{(cr)}$) of lactose and lactose/WPI mixtures were analyzed and determined by calculating the changes of c_w in DDI of each sample using derivative analysis (Yuan et al., 2011). The procedures used to obtain the first and the second derivative was as follows. Attempts to leave out noise and find the peak location, the a_w and c_w data derived from DDI were smoothed using LOESS (local polynomial regression fitting) smoothing (second-degree polynomial) with a span of 11 points using the *R* programme, version 3.2.3 (The R Foundation[®], Murray Hill, NJ, USA). The smoothed data set was fit using a smoothing cubic spline after which the first derivative of the fit was taken. The peak a_w of the 1st derivative function ($a_{wp}^{(cr)}$) based on smoothed DDI data was taken as acceleration point for

lactose crystallization. The smoothing and fitting procedures were repeated for the 1st derivative after which the 2nd derivative was obtained from the 1st derivative. Water sorption data showed that a substantial peak on the 2nd derivative developed with onset around the calorimetric T_g corresponding a_w , $a_{wo}^{(cr)}$ (Fig. 1A). The water plasticization to above the glass transition induced translational mobility of lactose. Such mobility with further water plasticization could increase free volume to provide water sorption sites and hydrogen bonding structuring of the lactose-water system to accommodate water with less direct lactose-lactose interactions. The programmed codes for achieving first and second derivative analysis in *R* programme were shown on Supplementary Information.

2.3. Dielectric analysis (DEA)

DEA was used to measure dielectric properties from the dielectric constant or permittivity (ϵ'), dielectric loss (ϵ''), and their ratio $\tan \delta = (\epsilon''/\epsilon')$ as a function of temperature. The ϵ' describes an alignment of dipoles and the ϵ'' describes an energy that is required to align dipoles (Talja & Roos, 2001). In the present study, the freeze-dried lactose and lactose/WPI at 7:3, 1:1 and 3:7 mass ratios were humidified for 120 h over saturated solutions of CH_3COOK , $MgCl_2$, and K_2CO_3 (Sigma Chemical Co., St. Louis, Mo., USA) to obtain respective water activities of 0.23, 0.33 and 0.44 a_w at

equilibrium in vacuum desiccators in incubators at storage temperature of 25 °C. Dielectric properties of both dry and humidified samples were analyzed using dielectric analyzer (DS6000, Triton Technology Ltd., UK), with titanium sample holders as the electrodes. The LCR meter (inductance, capacitance, and resistance; LCR-819) and DEA instrument were calibrated and zeroed with the open-short circuit of the electrodes before starting experiments. Samples were ground and approximately 600 mg samples were placed between parallel plate titanium capacitors (diameter = 33 mm) with the thickness less than 2 mm. Triplicate samples of each material were analyzed using dynamic measurements and recorded using Triton Laboratory software (version 1.0.330). Samples were analyzed in triplicate using dynamic measurements and scanned from ~ 60 °C below to over the T_g region with cooling rate of 5 °C/min and heating rate of 2 °C/min at frequencies of 0.5, 1.0, 5.0, 10.0 and 20.0 kHz. The measuring head was connected to a liquid nitrogen tank (1L; Cryogun, Brymill cryogenic systems, Labquip (Ireland) Ltd., Dublin, Ireland). As noted above, T_α determined from the temperature of ε'' at the peak were used to determine the relaxation times.

2.4. Strength analysis

The relaxation times and T_a corresponding to ε'' peak above T_g were modeled using the WLF equation (Eq. 1). The relaxation times were defined by frequency set in DEA measurements ($\tau = 1/2\pi f$). The WLF model constants C_1 and C_2 were derived from a plot of $1/\log(\tau/\tau_g)$ against $1/(T-T_g)$ using experimental τ with the assumption of $\tau_g = 100$ s at the calorimetric onset temperature of the T_g (Angell 2002). A decrease in the number of logarithmic decades for flow, e.g., that being critical for stickiness, could be used as the critical parameter, d_s , of Eq. (2) and the corresponding $T-T_g$ was defined as the strength of the solids, S . As the S values are given as temperature corresponding to a critical τ for a key amorphous component within a material, it also provides a measure of resistance to structural changes, i.e., the higher value of S refers to a stiffer system at a corresponding $T-T_g$.

$$\log\left(\frac{\tau}{\tau_g}\right) = \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \quad (1)$$

$$S = \frac{d_s C_2}{C_1 - d_s} \quad (2)$$

Where, T , T_g , τ , τ_g , C_1 and C_2 and d_s shown in Eq (1) and (2) refer to the experimental temperature, onset glass transition temperature, experimental structural relaxation time and structural relaxation time at the glass transition ($\tau_g = 100$ s), material-specific WLF constants and the decrease in the number of logarithmic decades for τ ($d_s = 4$ was used

for various biological materials as reported by Roos et al. (2015) and Fan and Roos (2016b), respectively.

2.6. Statistical analysis

The second derivative analysis of DDIs sorption data was carried out in *R* Programme and the strength analysis of dielectric α -relaxation associated relaxation times were calculated and fitted by using Microsoft Office Excel 2011 (Microsoft, Inc., USA). All measurements were repeated three times, as well as the average values with the standard deviation of triplicate measurements were calculated.

3. Results and Discussion

3.1. Dynamic Water Sorption

Table 1 and Fig. 2

The DDI for pure lactose ($a_w \leq 0.50$), WPI and lactose/WPI mixtures with the mass ratios of 7:3 ($a_w \leq 0.70$), 1:1 ($a_w \leq 0.80$) and 3:7 followed the typical sigmoid shape of water sorption isotherms (type II) in Fig. 1B, respectively. The fractional water sorption of components, exhibited by amorphous sugar/protein mixtures, has been

reported by previous studies (Roos & Potes, 2015). Similarly, the fractional water sorption properties were proved in DDIs as the sorbed water in amorphous lactose/WPI mixtures could be calculated as the sum of fractional quantities at $a_w \leq 0.44$ (Fig. 1B). However, if water sorption rates of components vary DDI data may reflect such differences. Fig. 2 gives the DDI water sorption and literature SSM data for freeze-dried lactose and lactose/WPI mixtures at 7:3, 1:1 and 3:7 mass ratios at 25 °C (Fan & Roos, 2015). The water contents in DDIs of lactose were lower than those of corresponding SSM isotherms (Fig. 2A). Such differences in the DDI sorption data reflected the non-equilibrium state of amorphous solids and the relatively short equilibration time in comparison to SSM giving a systematic error for the water content as full dehydration may not take place at low a_w . The SSM-isotherms comparable c_w data are shown on the DDIs of lactose/WPI mixtures at various protein contents (Fig. 2B-D). The DDI sorption data of pure amorphous WPI, however, showed shape-comparable sorption isotherms to corresponding SSM isotherms (Fig. 2E). Such similarity in water sorption by the two methods indicated that the amorphous WPI showed a slow equilibration reducing time to water vapor diffusion and water penetration during DDI sorption. The DDI sorption data for amorphous lactose leveled off at high water activities ($\geq 0.50 a_w$) as a result of lactose crystallization (Fig. 2A). In lactose/WPI systems lactose molecules form a continuous phase around WPI molecules, but WPI components may hinder diffusion of the noncrystalline lactose. In comparison to pure lactose, therefore, the presence of WPI in lactose/WPI mixtures

268 delayed crystallization and extended the sigmoid sorption behaviors to a higher a_w
269 range (Fig. 2B-C). This phenomenon agreed with previous studies, which indicated that
270 the crystallization of lactose could be delayed by the presence of polymeric
271 components (Silalai & Roos, 2011). As noted above, the presence of other components,
272 e.g., protein, with amorphous sugars, affected water sorption as well as the
273 crystallization as a result of water plasticization.

274
275 **Fig. 3**

276
277 The $a_w^{(cr)}$ values of amorphous lactose and lactose/WPI mixtures at each ratio are
278 shown in Table 1, respectively. Fig. 2F showed a linear relationship with high
279 correlation coefficient ($R^2 > 0.98$) for $a_w^{(cr)}$ values against lactose content of amorphous
280 lactose/WPI systems at 25 °C, which indicated that the $a_w^{(cr)}$ was that of the lactose
281 component rather than for the entire system although protein affected structural
282 relaxation times (Roos & Potes, 2015). In the present study, the $a_{wo}^{(cr)}$ was considered
283 as a critical a_w point for glass-forming lactose plasticized by water to flow and
284 accommodate increasing free volume and water uptake during DDI sorption process.
285 The $a_{wp}^{(cr)}$ was a turning point where the rate of water uptake became less than the rate
286 of lactose crystallization. Corresponding to previous X-ray study (Jouppila et al., 1997),
287 therefore, we assumed that the $a_{wo}^{(cr)}$ and $a_{wp}^{(cr)}$ were the onset and half-crystallinity

point of lactose crystallization, respectively. In the present study, the $a_{wo}^{(cr)}$ of pure amorphous lactose occurred at 0.381 a_w at 25 °C (Table 1). This result agreed with previous calorimetric studies that the glass transition of freeze-dried lactose after humidification at 0.44 a_w at room temperature was around 15 °C as well as the critical a_w of 0.37 of amorphous lactose (Fan & Roos, 2016a). Both onset and peak $a_w^{(cr)}$ values of lactose/WPI mixtures increased concomitantly with increasing protein content (Table 1). Fig. 3 gives a schematic diagram for the dynamic water sorption process of amorphous lactose and lactose/WPI mixtures. From I to II (Fig. 3A), the water sorbed by amorphous lactose could plasticize the structure of glass formers resulting in breaking the hydrogen bonds between lactose molecules and the relaxation times of amorphous lactose decreased (Slade et al., 1991). As a_w increased to above $a_{wo}^{(cr)}$, the mobilization of glass formers was strongly enhanced by water plasticization (Fig. 3A II-III). When the a_w exceeded $a_{wp}^{(cr)}$, the lactose crystallinity rapidly increased until most of lactose crystallized during the DDI sorption process (Fig. 3A III-IV). However, the presence of WPI hindered water plasticization effects as the $a_{wo}^{(cr)}$ increased in lactose/WPI mixtures (Fig. 3B II-III). Moreover, the $a_{wp}^{(cr)}$ of lactose/WPI mixtures increased concomitantly with the WPI content and delayed the lactose crystallization in mixtures (Fig. 3B III-IV). Therefore, the $a_w^{(cr)}$ values of the DDI data indicate the glass transition resulting in mobilization and crystallization of amorphous lactose in food and pharmaceutical materials.

3.2. Dielectric properties and T_α

Table 2 and Fig. 4

Fig. 4 shows the dielectric loss (ε'' peaks at a frequency of 1.0 kHz) for lactose and lactose/WPI mixtures with mass ratios of 7:3, 1:1 and 3:7 after storage below 0.44 a_w at 25 °C. Dielectric properties of the materials were affected by molecular interactions and water plasticization. The magnitude of the ε'' peak correlated directly to a_w of amorphous lactose at low water activities ($0.23 \leq a_w \leq 0.44$) as water content increased and plasticization enhanced the mobility of lactose molecules. This agreed with Silalai and Roos (2011) who reported that ε'' peaks found for skim milk powder increased in magnitude with increasing a_w (Fig. 4A). The ε'' describes an energy loss that is used by polar groups in materials under the alternating electric field. The lower levels of WPI containing lactose/WPI mixtures (≤ 30 %) showed higher magnitudes of ε'' peaks than pure lactose after humidification at the same a_w and 25 °C (Fig. 4B-D). Therefore, the ε'' data followed the amorphous lactose content of the mixtures as WPI and lactose exist in separate phases. Table 2 gives the T_α value of each material in dielectric analysis at 1.0 kHz, which occurred above the corresponding calorimetric onset T_g measured by differential scanning calorimeter (DSC) in agreement with Silalai and Roos (2011). The presence of water, in the present study, decreased the T_α values of amorphous lactose and lactose/WPI mixtures as the peak temperature of ε'' concomitantly

decreased with increasing a_w (Table 2). The T_α values of amorphous lactose could be significantly increased by WPI in lactose/WPI mixtures (Table 2). Lactose can be assumed to exist separated from protein. The frequency-dependent T_α indicated an apparent relaxation time of lactose in WPI mixtures. Water plasticization enhanced the molecular mobility of lactose molecules which consequently decreased the peak temperature of ε'' . However, the WPI contained in mixtures hindered the molecular mobility of lactose and increased the apparent relaxation times and T_α . In our previous studies, similarly, the presence of other components, i.e., water and protein, affected the structural relaxations, relaxation times and T_α of glass-forming sugars in freeze-dried sugars/protein systems based on dynamic-mechanical analysis (DMA) (Fan & Roos, 2016a,b).

3.3. Relaxation times and S parameter

Fig. 5

Both DEA and DMA measurements allowed determination of structural relaxation times from the α -relaxation data at various frequencies. The structural relaxation times can be related to stickiness characteristics of food powders as well as other mechanical

properties of food solids, such as the collapse of structure or viscosity and diffusion (Clerjon et al., 2003). Fig. 5 shows structural relaxation times from our experiments and literature (Fan & Roos, 2016a). The WLF-relationship of Williams et al. (1955) was developed on the basis that most inorganic and organic glass formers showed similar decreases in τ and viscosity over the temperature range of T_g to $T_g+100\text{K}$. The use of WLF-relationships often assumes that the structural relaxation time obtained using dielectric measurements reach 100 s at the calorimetric onset T_g (Angell, 2002; Roos et al., 2015). In the present study, the WLF-relationship with “universal” constants ($C_1 = -17.44$ and $C_2 = 51.6$) did not fit the experimental data but material-specific constants gave a good fitting performance for lactose and lactose/WPI mixtures at a_w below 0.44 and 25 °C (Fig. 5). Table 2 gives material-specific WLF constants for amorphous lactose and lactose/WPI mixtures obtained from structural relaxation times of the DEA and published DMA measurements. The material-specific C_1 for amorphous lactose increased concomitantly with a_w increasing, whereas both C_1 and C_2 decreased by the presence of WPI content at a_w below 0.44 (Table 2). It is important to note that fitting of the WLF model to experimental relaxation times may result in positive or negative values for the constants C_1 and C_2 (Roos & Drusch, 2015). In the present study, the C_1 and C_2 with negative values determined the downward concavity for WLF relationship, which showed the profiles for the decreases of relaxation times of amorphous lactose at temperatures above calorimetric T_g . Therefore, the material-specific WLF constants could be used to

describe material properties and structural relaxation processes of amorphous lactose at various water activities. The presence of other components, e.g., water and protein, affected the structural overall relaxation processes as well as apparent relaxation times of lactose/WPI mixtures.

The decrease of relaxation times to 10^{-2} corresponded to a decrease in viscosity from 10^{12} Pa s to 10^5 Pa s reaching critical viscosities for collapse and stickiness of amorphous food solids (Bellows & King, 1973; Downton, Flores-Luna, & King, 1982). Roos et al. (2015) recommended a WLF model-based strength analysis for amorphous sugars/protein systems. The S parameter for glass-forming components calculated by using material-specific WLF constants defined an allowable increase in temperature above the onset of the calorimetric T_g until $\tau = 0.01$ s. As the lactose and protein diffusion was uncoupled the S parameter followed relaxation times of amorphous lactose. Table 2 gives the S values of amorphous lactose and lactose/WPI mixture at low a_w based on the strength analysis using experimental structural relaxation times derived from DEA and published DMA data. In the present study, the S values of freeze-dried lactose with different water activities agreed with our earlier data (Fan & Roos, 2016a). The presence of water decreased the structural strength of amorphous lactose at a_w below 0.44, whereas the S values of lactose/WPI mixtures were significantly higher than was found for pure lactose (Table 2). As the S parameter

provides a measure of structural transformation, a low S value referred to a more rapid structural change. Such rapid changes occurred in the presence of water as the structural relaxations of amorphous lactose were enhanced by water plasticization. However, the relatively higher S exhibited by lactose/WPI mixtures indicated that the mixes were strengthened against structural deformation as protein offered a structural supporting effect. Therefore, the S parameters based on dielectric/mechanical relaxations can be used to describe compositional effects of amorphous food solids systems. Such data can be used to control shrinkage in dehydration and possibly rates of physicochemical changes in food storage.

3.4. Sorption-induced crystallization, relaxation times and S parameter

Fig. 6

The relationships between a_w and $T-T_g$ of amorphous lactose and lactose/WPI mixtures against their corresponding relaxation times are shown in Fig. 6A. The water-induced structural relaxations of food solids systems, observed in isothermal water sorption, are likely to correlate with crystallization above glass transition. The relaxation times of lactose dramatically decreased with increasing $T-T_g$ as the T_g was depressed by water

(Fig. 6A). The crystallization of lactose was initialized above $a_{wo}^{(cr)}$ and rapidly occurred along decreasing structural relaxation times during water sorption process. The water sorption-induced lactose crystallization could stop at 0.7 a_w based on the DDI sorption data, where the τ decreased approximately 4 logarithmic decades (Fig. 6A). As we expected, the $a_{wo}^{(cr)}$ for water-induced crystallization was delayed to occur at higher a_w in the presence of WPI (Fig. 6A). The decrease of structural relaxation times, $a_{wp}^{(cr)}$ and crystallization of amorphous lactose can be controlled by WPI during exposures to high humidities (Fig. 6A). Fig. 6B shows a plot of onset and peak $a_w^{(cr)}$ against S for anhydrous lactose and lactose/WPI mixtures. There was a linear relationship between $a_w^{(cr)}$ and S with high correlation ($R^2 > 0.97$). The pure lactose had a lower $a_w^{(cr)}$ and S value than WPI containing systems (Fig. 6B). This result indicated that the structural strength could be related to water-induced crystallization of amorphous sugars during isothermal water sorption. Therefore, we believe that the DDI provided parameters describe the structural changes and crystallization behavior of amorphous sugars during water plasticization. The S parameter could be used to estimate time-dependent water sorption-induced solid properties of amorphous food mixtures during storage at various water activities, i.e., structural transformations and deformation. Moreover, proteins as commonly used components could be used in food and pharmaceutical systems to control water sorption properties as well as structural relaxation rates and crystallization.

4. Conclusion

We have shown that the freeze-dried lactose and lactose/WPI mixtures have fractional water sorption properties. Water sorption-induced relaxations and crystallization were delayed in the presence of WPI in amorphous lactose/WPI mixtures. The T_α values of amorphous lactose in lactose/WPI mixtures at $a_w \leq 0.44$ were affected by the mixture composition, i.e., water, and WPI. The WLF analysis based S parameter with relaxation times data from DEA and DMA was dependent on mixture composition. It was used to interpret water sorption-induced crystallization of amorphous lactose in mixtures with WPI. The combination of dielectric and mechanical properties offers a new approach in understanding glass transition-related structural relaxations occurring in food processing and storage. Such information also advances innovations in food formulation through mapping of structural relaxation times of food components and their mixes.

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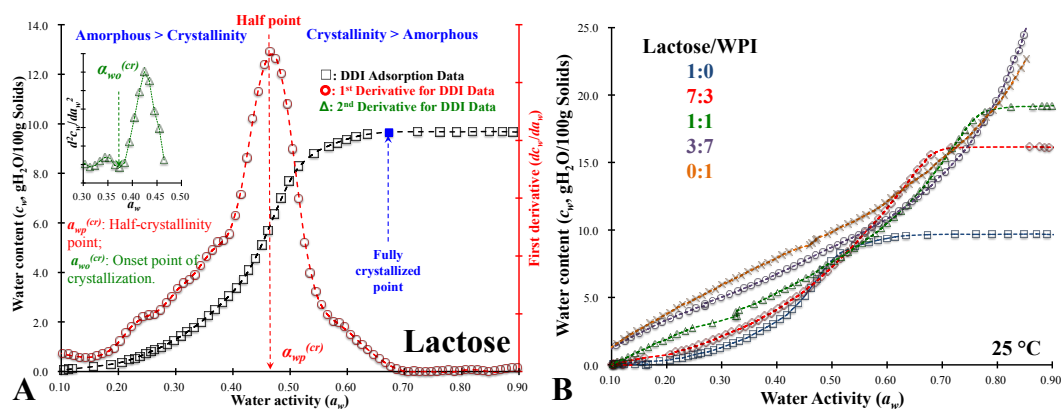


Figure 1. The $a_w^{(cr)}$ for freeze-dried lactose respectively taking the peak a_w of first derivative ($a_{wp}^{(cr)}$) and onset a_w of the second derivative ($a_{wo}^{(cr)}$) on DDI sorption data at 25 °C (A). B shows the DDI curves for lactose and lactose/WPI mixtures with 7:3, 1:1 and 3:7 mass ratios by running at 25 °C, respectively.

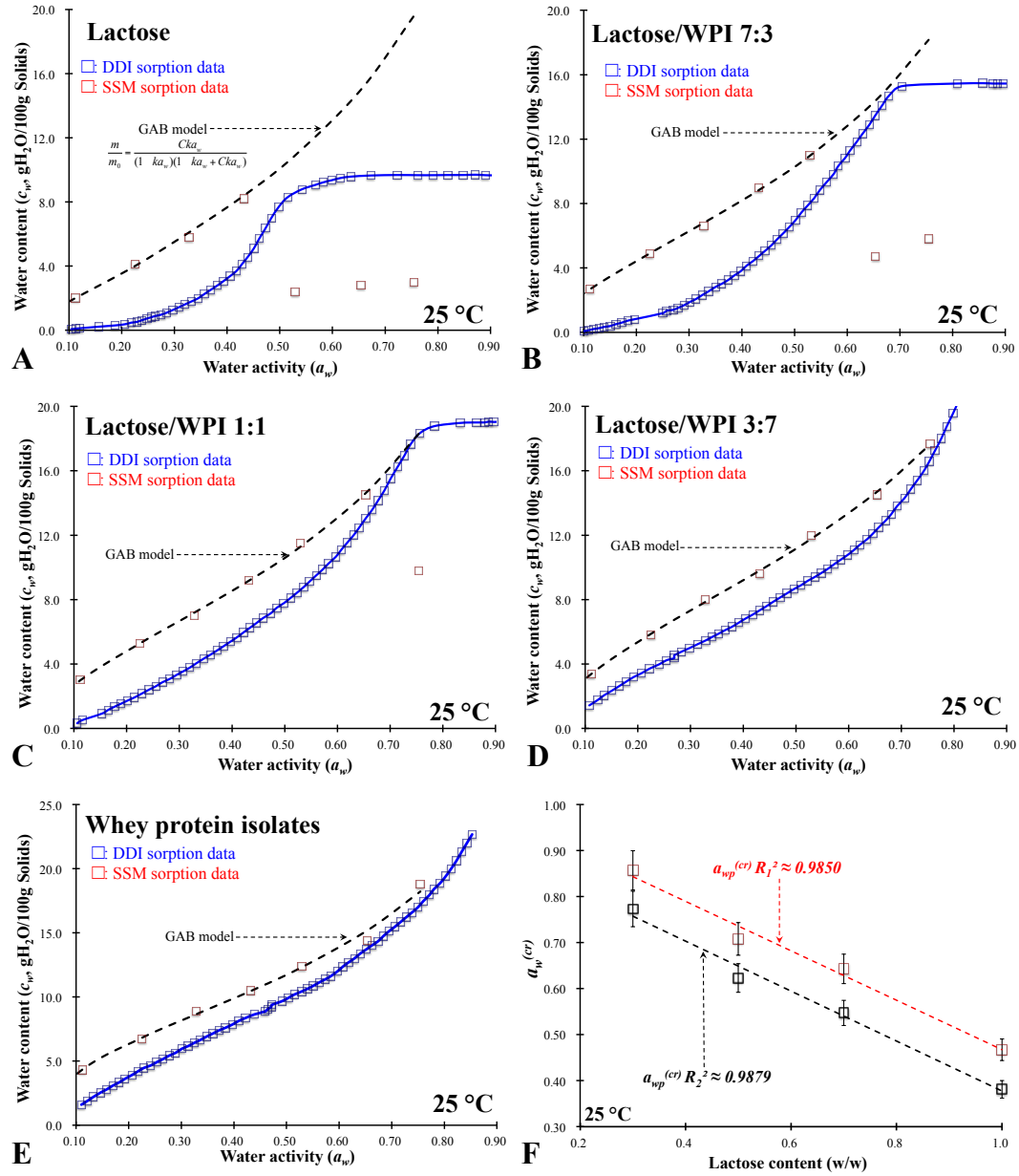


Figure 2. The comparison diagram between DDI and literature SSM data of freeze-dried lactose and lactose/WPI mixtures (7:3, 1:1 and 3:7, w/w) at flow rates of 300 ml/min at 25 °C (A-E). The $a_w^{(cr)}$ shows a highly linear relationship with lactose content ($R^2 > 0.98$) in lactose/WPI mixtures (F). The literature SSM sorption data were derived from Fan and Roos (2015).

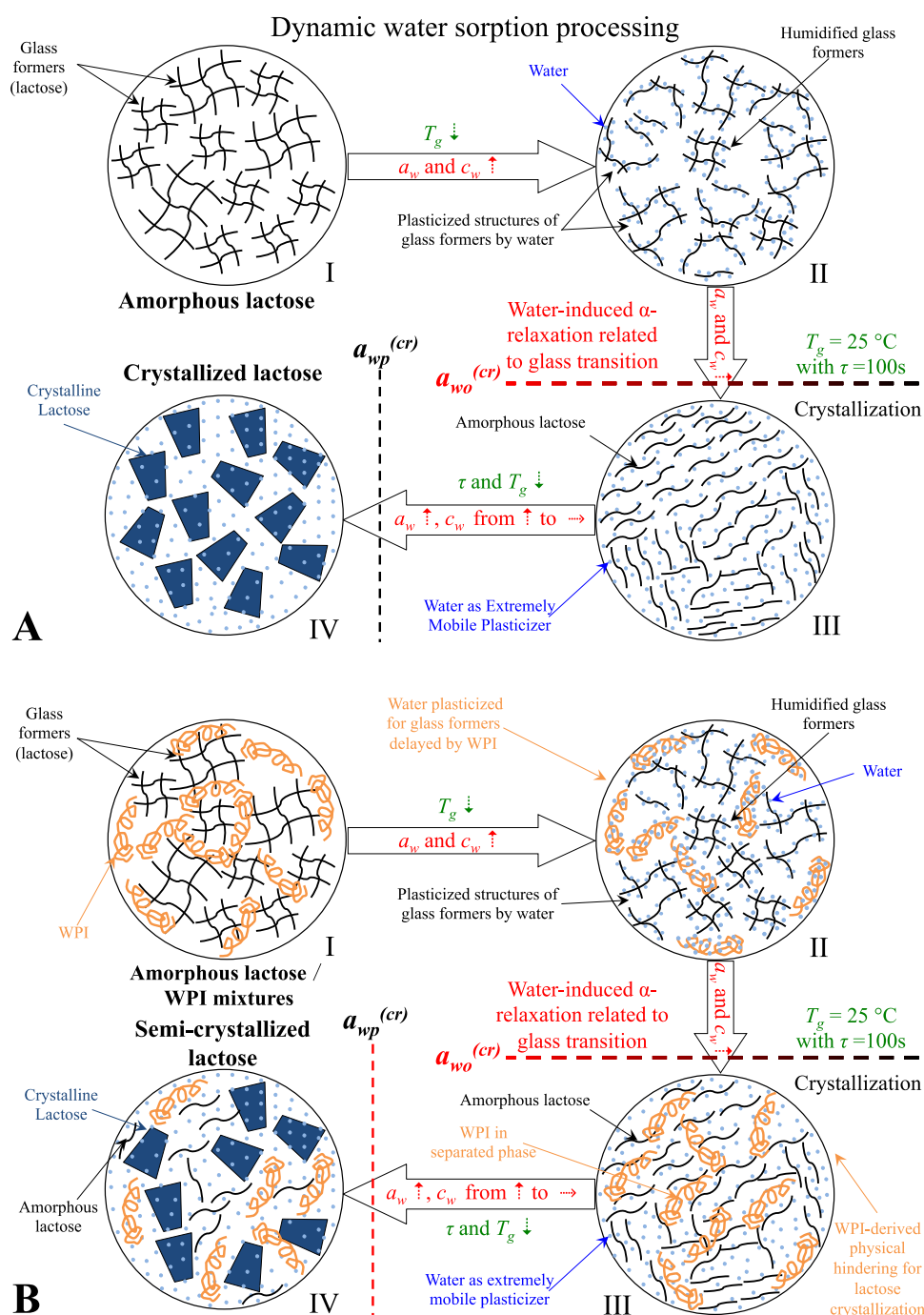


Figure 3. Schematic diagrams for water-induced α -relaxation and crystallization on amorphous lactose (A) and lactose/WPI mixtures (B) in dynamic water sorption processes, respectively. The symbols do not represent the real size and quantity of components.

Figure

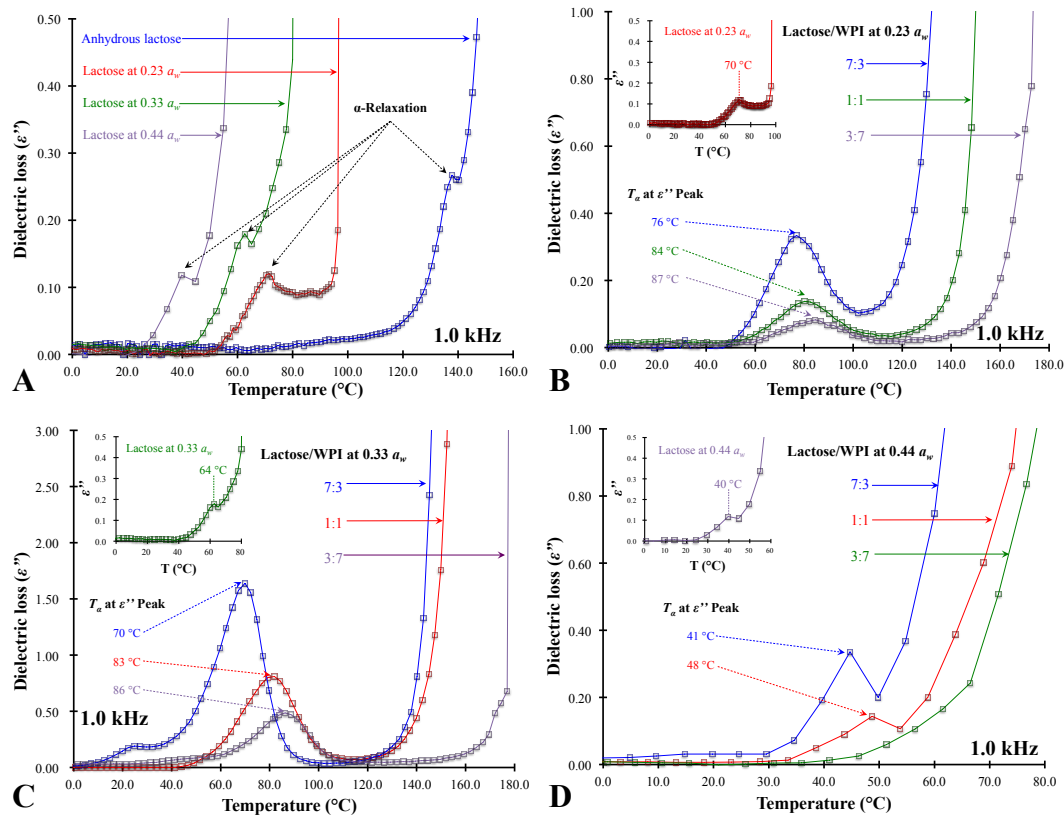


Figure 4. The DEA spectra and peak temperature of ϵ'' as T_α of amorphous lactose (A) and lactose/WPI mixtures with 7:3, 1:1 and 3:7 mass ratios after storage at $0.23 a_w$ (B), $0.33 a_w$ (C), and $0.44 a_w$ (D) under 25 °C.

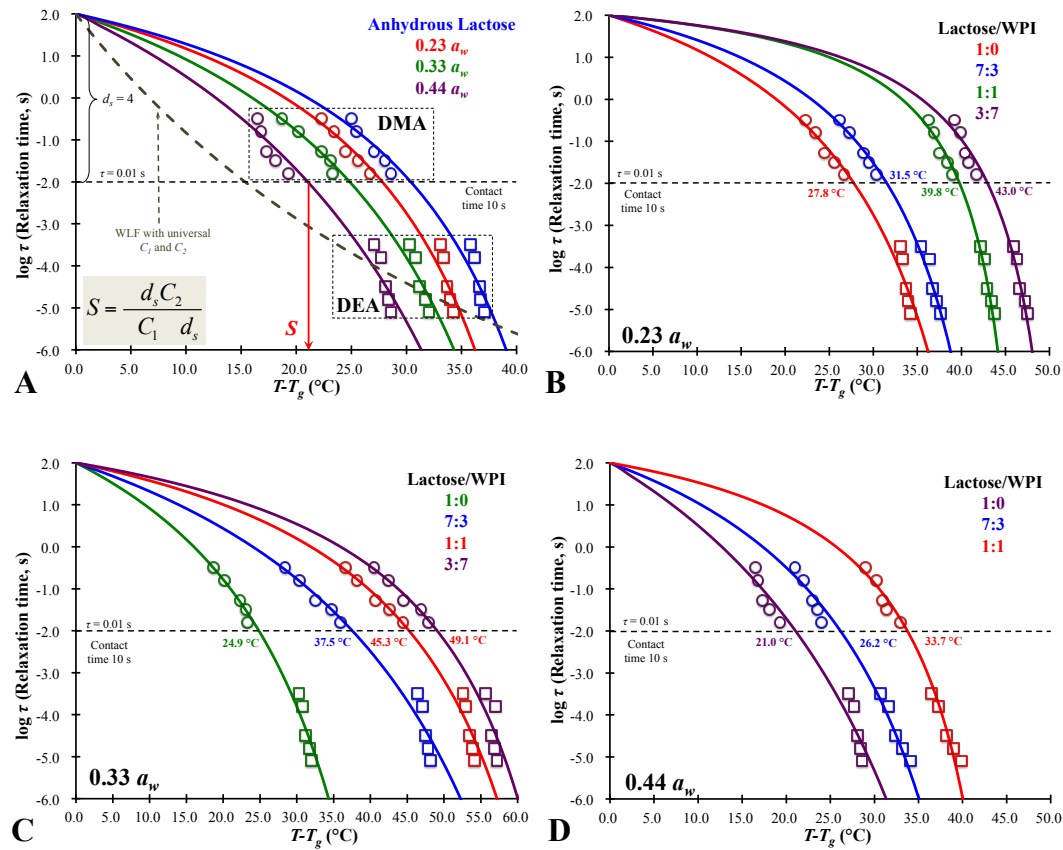


Figure 5. Strength parameters (S) of freeze-dried amorphous lactose at various water activities (0-0.44 a_w) (A), lactose/WPI mixtures at mass ratio of at 7:3, 1:1 and 3:7 at frequency of 1.0 kHz after storage at 0.23 a_w (B), 0.33 a_w (C) and 0.44 a_w (D) at $d_s = 4$ decreasing τ as measured using DEA and literature DMA (Fan & Roos, 2016c) down to 0.01 s. Such decrease in τ is known to result in particle stickiness and aggregation at a contact time of 10 s (Roos et al., 2015).

Figure

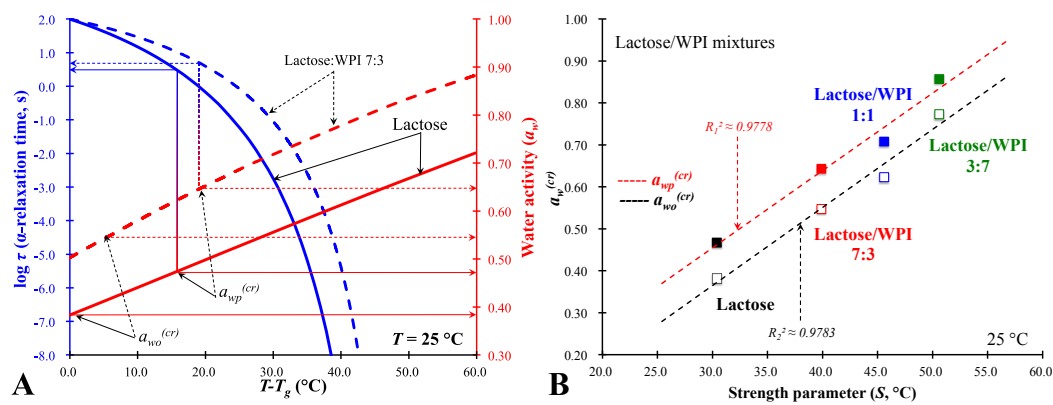


Figure 6. The relationship between a_w and $T - T_g$ of amorphous lactose and lactose/WPI mixture at 7:3 (w/w) with their corresponding relaxation times (A). B shows the relationship between strength parameter (S) and $a_w^{(cr)}$ for amorphous lactose and its WPI containing mixtures at 25 °C.

Figure Captions

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Table 2. The literature onset T_g , T_α at 1.0 kHz, material-specific C_1 and C_2 , and S for freeze-dried lactose, lactose/ WPI mixtures at solid ratios of 7:3, 1:1 and 3:7 after storage at low a_w (≤ 0.44) at 25 °C.

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Sample	Ratios	$a_{wo}^{(cr)}$	$a_{wp}^{(cr)}$
Lactose	-	0.381±0.010 ^a	0.467±0.003
Lactose/WPI	7:3	0.547±0.018	0.643±0.001
Lactose/WPI	1:1	0.623±0.028	0.708±0.006
Lactose/WPI	3:7	0.773±0.013	0.857±0.001

^a: Values are mean ± SD (n=3)

Table 2. The literature onset T_g , T_α at 1.0 kHz, material-specific C_1 and C_2 , and S for freeze-dried lactose, lactose/ WPI mixtures at solid ratios of 7:3, 1:1 and 3:7 after storage at low a_w (≤ 0.44) at 25 °C.

Sample	a_w	T_g	T_α	C_1	C_2	S
Lactose	0.00	105±3 ^a	138±2	3.19±0.31	-54.63±0.63	30.4±0.7
	0.23	40±2	72±1 ^b	3.47±0.23	-51.93±0.42	27.8±1.0
	0.33	30±3	64±3	4.93±0.19	-55.48±0.56	24.9±0.8
	0.44	14±1	40±1	7.66±0.45	-61.36±0.66	21.0±1.6
Lactose/WPI 7:3	0.23	40±1	76±1	2.38±0.33	-50.31±0.64	31.5±0.9
	0.33	30±1	70±1	5.15±0.21	-85.88±0.50	37.5±1.0
	0.44	13±1	41±3	4.13±0.35	-53.15±0.52	26.2±1.3
Lactose/WPI 1:1	0.23	41±1	84±1	0.98±0.43	-49.55±0.41	39.8±0.5
	0.33	30±2	83±1	2.87±0.44	-77.72±0.76	45.3±0.5
	0.44	14±2	48±5	1.83±0.25	-49.18±0.63	33.7±0.4
Lactose/WPI 3:7	0.23	41±2	87±0	1.07±0.38	-54.47±0.66	43.0±0.7
	0.33	30±3	86±4	2.30±0.29	-77.28±0.73	49.1±0.5
	0.44	13±2	N/A	-	-	-

^a: The onset T_g of lactose and lactose/WPI mixtures are derived from Fan and Roos (2016c); ^b: Values are mean ± SD (n=3);

R-code and dataset(s) (.ZIP)

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